

FLUID-MEDIATED ALTERATION ON 4 VESTA – EVIDENCE FROM ORTHOPYROXENE CLASTS IN HOWARDITES. D. W. Mittlefehldt¹, K. N. Johnson² and J. S. Herrin³, ¹Astromaterials Research Office, NASA/Johnson Space Center (david.w.mittlefehldt@nasa.gov), ²Dept. of Chemistry & Biochemistry, Arizona State University, ³ESCG, NASA/Johnson Space Center.

Introduction: The howardite, eucrite and diogenite (HED) meteorites represent the products of igneous processes and impact mixing on a differentiated asteroid. Eucrites are basaltic composition rocks that were formed as flows and as shallow and deep intrusive bodies. Some eucrites are cumulate gabbros. Diogenites are cumulate orthopyroxenites widely considered to be of deep crustal origin. Impact processes have excavated material from deep levels of the crust, and mixed it with surface rocks into a suite of polymict breccias. Howardites are one such rock type, being composed mostly of mixtures of clasts and mineral fragments of eucritic and diogenitic parentage [see 1]. The consensus view is that 4 Vesta is the parent asteroid of HED meteorites [2].

As part of a larger study of the record of impact mixing contained within howardites, we undertook an investigation of the compositions of orthopyroxene clasts in a suite of howardites [3]. We discovered a subset of orthopyroxene clasts in some howardites with unusual textural and compositional characteristics that are reminiscent of those previously observed in phenocrysts in a pyroxene-phyric melt clast in howardite EET 92014 [4]. The textural and compositional characteristics of the phenocrysts in this clast were interpreted as originating via interaction with an FeO-rich fluid phase [4].

The HED parent asteroid is commonly thought of as being volatile-poor and anhydrous [1]. However, some evidence for interaction with fluids has been found in a few HEDs [4-7], suggesting that at some point in the geologic evolution of 4 Vesta, fluid phase(s) may have been locally important. In order to improve our understanding of the role of fluids on 4 Vesta, we began a more detailed study of the anomalous orthopyroxene clasts. Herewith, we present our preliminary results.

Petrology and Mineral Composition: We have made petrographic observations and done electron microprobe analyses on orthopyroxene and pigeonite grains in 18 howardites. The majority of the grains show normal Fe/Mn-Fe/Mg behavior - little change in Fe/Mn with increasing Fe/Mg (inset, Fig. 1, view at 400x). This is expected for igneous partitioning in HED magmas crystallizing pyroxene as the dominant ferromagnesian phase [see 8, 9]. Several grains show anomalous excursions in Fe/Mn that are not systematic with changes in Fe/Mg (Figs. 1, 2).

Figure 1 shows a back-scattered electron image of an example grain fragment from EET 99400. Core compositions fall within the field of normal low-Ca pyroxenes from howardites (inset, view at 400x). The grain interior includes patches and veinlets of Fe-enriched pyroxene (light grey). Transects a and b through magnesian and ferroan zones show Fe/Mn excursions from the field of normal pyroxenes; up to ~47 from an initial ~29 for transect b.

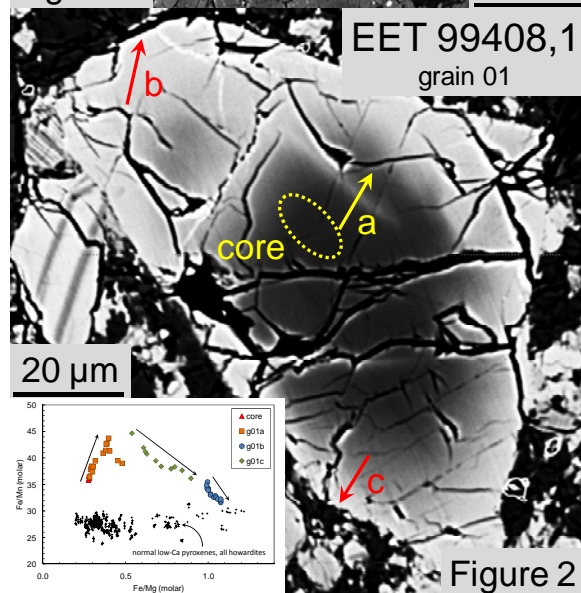
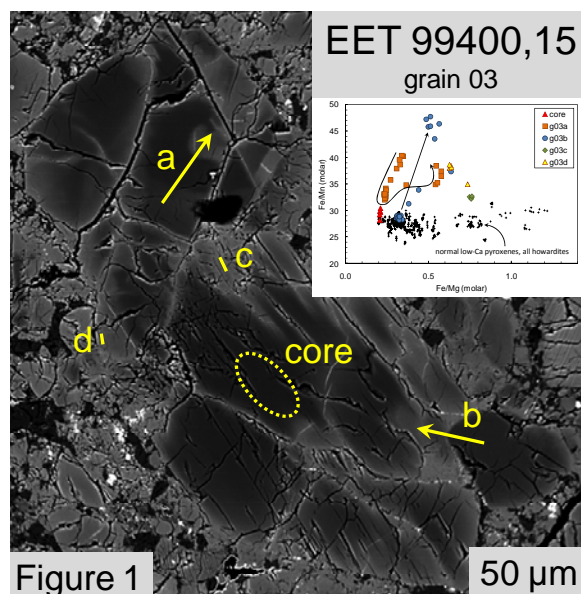


Figure 2 shows an example anomalous grain fragment from EET 99408. Transect a shows increasing

Fe/Mn going from magnesian to ferroan pyroxene, while transect b shows decreasing Fe/Mn as compositions become increasingly ferroan at the grain rim (view inset at 400x). Transect c shows that the most ferroan rim composition has a nearly normal Fe/Mn.

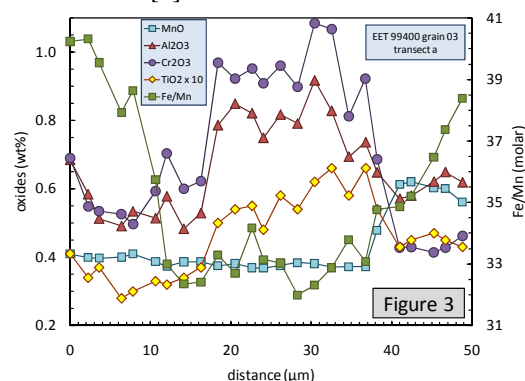
Discussion: Three of the howardites we have investigated thus far contain grains with strongly anomalous Fe/Mn regions – EET 99400, EET 99408, and EET 83376. Pairing has been suggested based on petrology for EET 99400 and EET 99408; no pairings have been suggested for EET 83376. SAN 03472 contains some low-Ca pyroxene grains that show slight Fe/Mn anomalies. We have not found anomalous grains in the other howardites we have examined.

Textural evidence indicates that development of the anomalous Fe/Mn regions occurred prior to incorporation into the current matrix. We commonly observe Fe-rich rims on magnesian low-Ca pyroxenes generated by thermal metamorphism in the ferroan environment of the current matrix. Such rims are more ferroan than the high Fe/Mn regions, yet have normal Fe/Mn (transect c, Fig. 2, inset). Textural evidence does not indicate whether the anomalous regions were developed while the grains were in their diogenite parent rocks or while contained in an intermediary breccia.

The minor element contents give evidence for possible redistribution of some non-quadrilateral components in the pyroxenes accompanying development of some of the anomalous Fe/Mn regions. EET 99400 grain 03 transect a started in a region with Fe/Mn ~41, went through a slightly more magnesian region with Fe/Mn ~33, and ended in a more ferroan region with Fe/Mn ~38 (Fig. 1). Element profiles along this transect show depletions in Al_2O_3 , TiO_2 and Cr_2O_3 in the high Fe/Mn regions compared to the central region with lower Fe/Mn (Fig. 3). The MnO content is uniform up until the transect end where the final Fe/Mn excursion occurs. Here MnO increases. The variation in Fe/Mg (Fig. 1) is accomplished through simultaneous decrease in MgO and increase in FeO; CaO does not appreciably vary. Not all Fe/Mn excursions are accompanied by depletions in minor elements.

Anomalous Fe/Mn variations in low-Ca pyroxene were noted along cracks and healed cracks in phenocrysts in an impact-melt clast in howardite EET 92014 [4] (not paired with the howardites studied here). This compositional anomaly was ascribed to fluid-mediated Fe metasomatism. Subsequently, additional evidence for metasomatism (quartz veinlets) has been found in the cumulate eucrite Serra de Magé and ascribed to deposition from liquid water solutions [5]. Evidence for metasomatism in the form of Fe-enrichment along cracks, deposition of ferroan olivine, troilite and calcic plagioclase, and depletions of Al in pyroxene has been

found in several basaltic eucrites [6, 7]. An aqueous fluid is considered a likely agent of metasomatism in these meteorites [7].



Igneous processes did not produce the Fe/Mn anomalous regions. Igneous processes do not efficiently fractionate FeO from MnO, leaving the Fe/Mn ratio nearly constant during crystallization [8, 9]. Texturally, the anomalous regions are randomly distributed in the grains, often in irregular patches or thin, vein-like zones, and do not show a distribution that can be interpreted as resulting from original crystallization. A more likely origin is as a result of fluid-mediated metasomatism at some stage in the history of the grains, but before incorporation in the current matrix. We have yet to identify the fluid phase or its source, but H_2O is the most plausible agent.

Conclusions: Low-Ca pyroxene clasts in some howardites show localized internal zones with anomalously high Fe/Mn ratios. These anomalous regions predate incorporation in the current matrix, but we have not yet determined when they were formed. Depletions in Al_2O_3 , TiO_2 and Cr_2O_3 accompany the Fe/Mn anomalies in some cases, but not all. The Fe/Mn change is mostly accomplished through a molar 1-to-1 swap of FeO for MgO in the pyroxenes along with non-systematic changes in MnO. These compositional anomalies were imposed by fluid-mediated metasomatism by a fluid phase, quite likely H_2O .

References: [1] Mittlefehldt D. W. et al. (1998) *Rev. in Mineral*, 36, chapter 4. [2] Drake M. J. (2001) *Meteoritics & Planet. Sci.*, 36, 501-513. [3] Johnson K. N. et al. (2011) *LPS XLII*, this conference. [4] Mittlefehldt D. W. and Lindstrom M. M. (1997) *Geochim. Cosmochim. Acta*, 61, 453-462. [5] Treiman A. H. et al. (2004) *Earth Planet. Sci. Lett.*, 219, 189-199. [6] Schwartz J. M. & McCallum I. S. (2005) *Am. Min.*, 90, 1871-1886. [7] Barrat J.-A. (2011) *Geochim. Cosmochim. Acta*, submitted. [8] Mittlefehldt D. W. (1990) *Geochim. Cosmochim. Acta*, 54, 1165-1173. [9] Mittlefehldt D. W. (2005) *Meteoritics & Planet. Sci.*, 40, 665-677.